

forming an acid manganese sulfate solution;

purifying the acid manganese sulfate solution; and

electrolytically oxidizing the manganese sulfate solution.--

### **REMARKS**

Claim 15 has been canceled. Claims 1-12, 16-30 and 32-34 remain active in the case. Reconsideration is respectfully requested.

### **Claim Amendments**

The language of all of the claims has been amended to indicate that the manganese oxide ore is, in fact, a manganese dioxide ore. Support for this change, for instance, is found at page 29, line 4 where the amending phrase is recited. Further, the ores identified as pyrolusite and psilomelane at page 13, line 5 of the specification are well known manganese dioxide ores. Reference in this regard is made to pages 972 and Table 2, page 975 of the attached article "Manganese Ore Used For Production Of High Carbon Ferromanganese" submitted to the Office and identified on Form 1449.

Claims 7 and 10 have been amended by limiting the reducing gases to hydrogen, carbon monoxide and methane.

Further, Claim 9 has been amended by including the limitation of Claim 2 therein. No new issues are believed to have been raised by the amendments that have been made. Entry of the amendments is respectfully requested.

### **Claim Rejection, 35 USC 112, First Paragraph**

As to the matter of the term which excludes molecular oxygen from the present process

claims, applicants have deleted the phrase objected to and have amended Claims 7 and 10 to recite that the reducing gas is at least one gaseous reducing agent selected from the group of gaseous reducing agents already recited in the claims or is a combination with the at least one reducing agent with an inert gas. The inert gas aspect of the invention is the feature of the present process set forth in Claim 15 which has been canceled. Further, the reducing gas is limited to one of the two recited groups by use of the phrase "consisting of" which is consistent with applicants' position on the record that the reducing gas does not contain molecular oxygen.

Accordingly, since the amendment to Claims 7 and 10 more clearly eliminates molecular oxygen from the reducing gas employed in the present process without introducing new matter into the case and without raising new issues, entry of the amendments to Claims 7 and 10 is respectfully requested.

Claim Rejection, 35 USC 112, Second Paragraph

The issue raised with respect to Claim 9 is obviated by the amendment made to the claim which simply deletes the word objected to from the claim. Entry of the amendment is respectfully requested.

The present invention relates to a treated manganese ore from which manganese sulfate is derived by which electrolytic grade manganese dioxide is prepared. The treated manganese ore is of exceptional purity, as stated in Claim 1, having a degree of manganese dissolution of 98.0 % or higher based on the manganese content of the treated ore. The process by which the treated ore of the invention has the advantages of reducing the amount of slag in the production step and also reduces the potassium content of the ore which is important in preparing a product which can be used to prepare manganese dioxide of high purity for use in electrolytic applications.

The treated ore of the invention is obtained by subjecting an appropriate manganese ore to reduction by contact with at least one reducing gas that consists of a gaseous reducing agent of a combination of the gaseous reducing agent with a diluent of an inert gas. The amount of the reducing gas used ranges from 1.0 to 2.0 times the theoretical amount necessary to reduce the manganese ore. Another embodiment of the process is that following the reduction treatment of the ore, the reduced ore is immersed in water having a temperature of 70° C to the boiling point at atmospheric pressure as embodied in Claim 10.

Claims 1-9 and 15-22 stand rejected based on 35 USC 103(a) as obvious over Welsh, U. S. Patent 3,375,097. This ground of rejection is respectfully traversed.

As stated on the record previously, Welsh teaches the reduction of manganese ore to MnO with no requirement for the production of a manganese ore which is able to result in an exceptionally pure manganese oxide product useful in electrolytic applications. There thus is no teaching or suggestion in the patent of a treated manganese ore having the minimum 98.0 wt % dissolvability in sulfuric acid which characterizes the treated manganese ore of the invention. Thus, Claim 1 is not rendered obvious by Welsh.

As to the matter of reducing manganese ore by the process disclosed in Welsh, it is clear from a consideration of the reference that a process is disclosed therein which is comparatively complicated in comparison to that which is presently claimed. As described in Claim 1 of the patent, the method of reduction of the reference requires the passage of a methane-rich hydrocarbonaceous gas-air mixture of a specified ratio of air to methane, first through a body of manganese ore whose "oxide of manganese content is in the form of MnO." At the temperature in this bed which ranges from 1000° F to about 2000° F, the air/methane mixture undergoes conversion by cracking of the methane to an atmosphere containing molecular hydrogen and CO. The MnO in the first bed of the process acts as a catalyst for this conversion. As shown in Fig.

5 of the reference, the manganese ore subjected to this particular reduction treatment, in coming into contact with the cracked gaseous product, also is subjected to contact with oxygen in the air component of the gas which causes an oxidation on the surface of the ore. Because of this surface oxidation, one of skill in the art expects that the manganese ore exhibits a reduced degree of manganese dissolution in sulfuric acid and thereby cannot reach the degree of manganese dissolution of 98.0 % by wt or higher of the present claims. This degree of dissolvability is achieved in the present invention because exposure of the manganese ore to oxygen containing gas does not occur. Thus, the process of reduction in Welsh in which the manganese ore is kept in contact with oxygen until the stage of immersion of the ore in water is not the same as that employed in the present invention.

As the reducing gas continues to flow through the ore bed, the hot CO and H<sub>2</sub> containing gas passes through a body or bed of unreduced manganese ore to reduce the ore therein to MnO. Clearly, this process is not that which is presently claimed which simply requires the passage of a gaseous reducing agent selected from the group identified in the claims through a manganese ore bed at a temperature of 400° C to 790° C. The present process not only does not require a conversion of methane gas to a gas mixture containing both CO and H<sub>2</sub> and further which does not require a bed of MnO in an ore pile prior to a bed of unprocessed manganese ore, but also excludes these aspects of the process of the patent by the limiting transitional language employed in the present process claims. Accordingly, Welsh does not obviate the invention as claimed and withdrawal of the rejection is respectfully requested.

Claims 1-6 stand rejected based on 35 USC 103(a) as obvious over El Tawil, U. S. Patent 4,985,216, Kane et al, U.S. Patent 3,810,827 or Barner et al, U.S. Patent 4,044,094. This ground of rejection is respectfully traversed.

As indicated by applicants' representative at the interview, the El Tawil patent discloses

a process for treating a Mn-Ag ore for the recovery of silver values from the ore. (See, for example, Claim 1 and column 5, lines 40-42) In the first step of the process the ore is subjected to roasting in the presence of one of the hydrocarbon reducing gases disclosed therein to reduce the  $\text{MnO}_2$  content to the desired level and then silver is recovered by hydrometallurgical techniques (col 3, lines 1-12). As disclosed in column 4, lines 19-37, the reduced ore is first subjected to leaching with the likes of sulfuric acid to remove manganese values therefrom. Apparently thereafter by some means the manganese oxide which is obtained is treated to form a manganese sulfate solution in turn to make an electrolytic grade manganese dioxide. Thus, the route employed by the patent to prepare a grade of manganese oxide acceptable from which to obtain an electrolytic grade of  $\text{MnO}_2$  is quite different from the method of production of the process claim embodiments of the present invention. Further contrary to the remarks by the Examiner at page 8, lines 13-15, El Tawil does not simply teach the treatment of a manganese ore with a reducing gas to prepare a grade of manganese oxide which in and of itself is acceptable as a material from which to prepare electrolytic grade manganese dioxide. Withdrawal of the reference is respectfully requested.

As to the Kane patent, it is obvious from the fact that because  $\text{SO}_2$  has been eliminated as a gaseous reducing agent from the present process, there is a clear line of distinction between the present invention as claimed and the Kane disclosure.

Applicants also emphasize another significant point of distinction between the present process and that of the patent which is that the present process requires the treatment of a manganese dioxide ore while it is clear that the reference does not. That is, as disclosed on page 13 of the present specification, pyrolusite and psilomelane are preferred ores of the present process. These ores are readily available. In the examples of the present application, manganese dioxide ores or 52.15 % by wt and 52.2 % by wt manganese dioxide are employed. These ores

are described in the “Manganese Ore Used For Production Of High Carbon Ferromanganese” publication mentioned above. (Refer in particular to Table 2 of the publication which discloses  $\text{MnO}_2$ ,  $\gamma\text{-MnO}_2$  and  $\delta\text{-MnO}_2$  containing ores from Brazil, Ghana and Australia.) It is normally presumed that the ores used in the present invention have a manganese content of 42.17 % or more and an iron content of 5.48 % or less. On the other hand, as disclosed in Table 1 of page 1 of Kane, the manganese nodules disclosed in Kane have a manganese content as low as 22.33 % or less and an iron content as high as 9.06 % or more. Thus, the manganese nodules used in the process of Kane are of a composition quite different than the manganese ore employed in the present invention, which means that the properties of the reduced ore, particularly the dissovability of the reduced ore in acid, are quite different than the dissolution characteristic of the reduced ore of Kane in acid. Withdrawal of the patent disclosure is respectfully requested.

As is clear from a consideration of Claims 7 and 10, the claims are limited to a method of producing a treated manganese ore by directly subjecting a manganese ore to a reducing gas of hydrogen, carbon monoxide or methane under the stated temperature condition. On the other hand, the Barner et al patent discloses a several stage process of treating manganese nodules for the purpose of removing metal values from the nodules including copper, nickel, cobalt and molybdenum. After deep sea manganese nodules are initially dried, the patent teaches that the dried nodules are subjected to a calcination in order to reduce the  $\text{MnO}_2$  to first  $\text{Mn}_2\text{O}_3$  and then to  $\text{Mn}_3\text{O}_4$  (see col 4, lines 39-65). Thereafter, the  $\text{Mn}_3\text{O}_4$  is treated in a reducer. The treatment is a fluidization of the  $\text{Mn}_3\text{O}_4$  in a reducer with a synthesis gas ( $\text{CO}$  and  $\text{H}_2$ ) which produces a  $\text{MnO}$  product. Clearly, this process of obtaining a  $\text{MnO}$  material is not the direct process of the present process claims in which in one step the manganese dioxide ore is directly reduced to  $\text{MnO}$  by reduction with a gaseous reducing agent that is hydrogen, carbon monoxide or methane at elevated temperature, thereby directly forming a manganese ore product that has the stated

manganese dissolvability of at least 98 % based on the manganese content of the treated manganese ore.

As in the case of the Kane reference, the manganese nodules that are used in the patent are quite different in manganese content from the manganese dioxide ore employed in the present process. Typically, the ore of the present process has a manganese content of 42.17 % or more and an iron content of 5.48 % or less. On the other hand, in Barner the nodules have a manganese content as low as 10.0 to 40.0 % and an iron content as high as 4.0 to 25.0 %. Because of these compositional differences, it is believed that ultimately the dissolvability properties of the reduced ore of the patent would be quite different from the reduced ore of the present invention. Moreover, Accordingly, withdrawal of the rejection of the indicated claims based on Barner is respectfully requested.

Claims 1-12 and 15-30 stand rejected based on 35 USC 103(a) as obvious over Barner et al, U.S. Patent 4,044,094. This ground of rejection is respectfully traversed.

The Examiner contends on page 5 of the Office Action that Barner teaches or suggests the present direct process of producing a treated ore is obvious because the process of the patent is the same as that which is presently claimed. However, as should be evident from the discussion above, the process of treating an ore in the patent is at least a three stage process in which an ore is first dried, and then the dried ore is passed to a calciner where the ore is heated in an atmosphere that has an oxygen partial pressure of 0 to 0.07 atm with the result that the ore is thermally decomposed first to  $Mn_2O_3$  and then at elevated temperature the  $Mn_2O_3$  is converted to  $Mn_3O_4$ . In the last step of the process, the  $Mn_3O_4$  is heated in a reducer in the presence of a synthesis gas to produce MnO. Thus, the patent discloses a staged reduction of manganese ore which clearly is not embraced by the process language of present Claims 7 and 10. Further, as to the product of present Claim 1, the patent is totally silent as to a treated manganese ore product

which has a dissolvability of at least 98 %. In fact, the product of the decomposition process of the patent is MnO which does not qualify as the treated manganese oxide product of the present invention. Accordingly, the Barner patent does not render the present claims obvious and withdrawal of the ground of rejection is respectfully requested.

Claim 34 stands rejected based on 35 USC 103(a) as obvious over Takehara, U. S. Patent 5,746,902 or Andersen et al, U.S. Patent 6,214,198 or Riggs, U.S. Patent 4,477,320. This ground of rejection is respectfully traversed.

As argued previously with respect to Claim 34, the claimed electrolytic manganese dioxide is, in fact, dependent on the reduced ore or reduced treated ore of Claim 1 or 5. This product has a very high degree of sulfuric acid dissolution of 98 % by wt or higher and even 99 % by wt or higher. Accordingly, when a manganese dioxide prepared by the process of the invention is employed in the process steps of Claim 34, the amount of slag which is generated can be reduced by a factor of 1/3 to 1/4 which reduces the load on the environment and reduces the concentration of potassium impurity in the electrolytic product manganese dioxide. This fact is shown in Table 1 of the specification where 6 examples within the scope of the invention of treated manganese ore have much lower potassium contents than the treated ores of Comp. Exs. 2 and 3, which examples do not conform to the limitations of the present process claims. On the other hand, none of the cited and applied patents teach the treated manganese oxide material of the present claims as described above and therefore they could not possibly and do not suggest the claimed electrolytic grade manganese dioxide of present Claim 34. Accordingly, the rejection based on the cited and applied patents is believed overcome and withdrawal of the same is respectfully requested.

Claims 32 and 33 stand rejected based on 35 USC 103(a) as obvious over El Tawil, U. S. Patent 4,985,216, Sasaki, U.S. Patent 3,667,906, Kane et al, U.S. Patent 3,810,827, Barner et

al, U.S. Patent 4,044,094 or Welsh, U. S. Patent 3,375,097 further in view of Bowerman et al, U.S. Patent 4,489,043, Takehara, U. S. Patent 5,746,902, Andersen et al, U.S. Patent 6,214,198, Andersen et al, U.S. Patent 4,948,484 or Riggs, U.S. Patent 4,477,320. This ground of rejection is respectfully traversed.

As stated on the record above, none of the El Tawil, Sasaki, Kane et al, Barner et al, or Welsh patents show or suggest a treated manganese ore which has the specific dissolvability requirement of the present claims. Yet, it is distinctly this material, as discussed above, that provides important advantages when for the preparation of an electrolytic manganese dioxide material. Moreover, although the Bowerman et al, Takehara, Andersen et al, Andersen et al, and Riggs patents disclose the electrolytic oxidation of manganese sulfate to electrolytic grade manganese oxide, the amount of slag generated in these processes can not be reduced to the low levels achieved in the present invention which uses the claimed treated manganese ore of the invention. Moreover, the prior art processes do not result in the reduced concentration levels of potassium impurity in the desired manganese dioxide product in comparison to the reduced potassium levels achieved in the present invention as seen above.

In this connection, applicants believe the Examiner errs when he states that the primary patents teach or suggest the presently claimed product and the process embodiments of producing a treated manganese ore for the reasons discussed above. Thus, a process of producing an electrolytic grade manganese dioxide would not be obvious in view of the art which does not teach or suggest the treated manganese dioxide of Claim 1, nor the process of preparing a treated manganese ore of Claim 7. Accordingly, the stated ground of rejection is believed obviated and withdrawal of the rejection is respectfully requested.

It is now believed that the application is in proper condition for allowance. Early notice to this effect is earnestly solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.



Norman F. Oblon  
Attorney of Record  
Registration No.: 24,618

Frederick D. Vastine, Ph.D.  
Registration No.: 27,013



**22850**

TEL: 703-413-3000  
FAX: 703-413-2220

**MARKED-UP COPY OF AMENDMENT UNDER 37 C.F.R. §1.116**

**IN THE CLAIMS**

Please cancel Claim 15.

Please amend 1-12, 16-30 and 32-34 as follows:

*Sub C1*  
*B1*  
~~1. (Amended) A treated manganese dioxide ore for use in producing manganese sulfate therefrom, said treated ore having a degree of manganese dissolution of 98.0 % by weight or higher based on the manganese contained in the treated manganese dioxide ore when dissolved in sulfuric acid.~~

~~2. (Amended) The treated manganese dioxide ore of Claim 1, which has a degree of manganese dissolution of 70 % by weight or higher based on the iron contained in the treated manganese dioxide ore when dissolved in sulfuric acid.~~

*B2*  
~~3. (Amended) The treated manganese dioxide ore of Claim 1, wherein the ratio of the amount of potassium soluble in sulfuric acid to that of manganese contained in the treated manganese dioxide ore by weight is 0.001 or lower.~~

*Sub C1*  
~~4. (Amended) The treated manganese dioxide ore of Claim 1, which is prepared by contacting a manganese dioxide ore with a reducing gas at a temperature ranging from 400 to 790° C.~~

*B3*  
~~5. (Amended) A treated manganese dioxide ore [obtained] prepared by immersing the treated manganese dioxide ore of Claim 4 in water having a temperature [of] ranging from 70° C to the boiling point thereof as measured at atmospheric pressure.~~

*Sub C1*  
~~6. (Amended) The treated manganese dioxide ore of Claim 1 or 5, which has a particle~~

B3  
SUB C1  
size of 500  $\mu\text{m}$  or smaller.

7. (Twice Amended) A process for producing the treated manganese dioxide ore of Claim 1, which [comprises] consists essentially of:

B4  
SUB C1  
contacting a manganese dioxide ore with a reducing gas consisting of at least one gaseous reducing agent or a combination of at least one gaseous reducing agent diluted with an inert gas, said gaseous reducing agent being [that does not contain oxygen and which contains at least one material] selected from the group consisting of hydrogen, carbon monoxide[, sulfur dioxide, hydrogen sulfide] and methane in an amount ranging from 1.0 to 2.0 times the theoretical amount required to reduce the manganese dioxide ore at a temperature ranging from 400 to 790° C, thereby preparing said treated manganese dioxide ore from which manganese sulfate is produced.

B5  
SUB C1  
8. (Amended) The process for producing a treated manganese dioxide ore of Claim 7, wherein the manganese dioxide ore is pulverized to a particle size of 500  $\mu\text{m}$  or smaller before the reduced ore is obtained therefrom.

B6  
SUB C1  
9. (Twice Amended) The process for producing a treated manganese dioxide ore of Claim 7, wherein the manganese dioxide ore is kept in contact with the gaseous reducing [gas] agent at a temperature ranging from 400 to 790° C for a necessary period [necessary] to [sufficiently reduce the] produce said manganese dioxide ore [with a reducing gas] of which the iron dissolution degree is 70 % or higher by weight when said manganese dioxide ore is dissolved in sulfuric acid.

10. (Twice Amended) A process for producing the treated manganese dioxide ore of Claim 1, which [comprises] consists essentially of:

contacting a manganese dioxide ore with a reducing gas consisting of at least one gaseous reducing agent or a combination of at least one gaseous reducing agent diluted with an inert gas, said gaseous reducing agent being [that does not contain oxygen and which contains at least one

material] selected from the group consisting of hydrogen, carbon monoxide[, sulfur dioxide, hydrogen sulfide] and methane in an amount ranging from 1.0 to 2.0 times the theoretical amount required to reduce the manganese dioxide ore at a temperature ranging from 400 to 790° C; and immersing the reduced ore obtained in water having a temperature ranging from 70° C to the boiling point thereof as measured at atmospheric pressure, thereby preparing said treated manganese dioxide ore from which manganese sulfate is produced.

B6  
11. (Amended) The process for producing the treated manganese dioxide ore of Claim 10, which further comprises washing the reduced ore obtained.

Sub C1  
12. (Amended) The process for producing the treated manganese dioxide ore of Claim 10, which further comprises washing and then filtering the reduced ore obtained.

16. (Amended) The process for producing the treated manganese dioxide ore of Claim 7, wherein the time period of the contact of the reducing gas with the manganese dioxide ore [is] ranges from 20 to 120 minutes.

B7  
Sub C1  
17. (Amended) The process for producing the treated manganese dioxide ore of Claim 7, wherein the contact of the reducing gas with the manganese dioxide ore is conducted continuously with a rotary kiln.

B8  
Sub C1  
18. (Amended) The process for producing a treated manganese dioxide ore of Claim 17, wherein the rotary kiln has a cylindrical or prismatic shape.

B9  
Sub C1  
19. (Amended) The process for producing a treated manganese dioxide ore of Claim 17, wherein the rotary kiln is equipped with a device for mixing the ore with the reducing gas.

Sub C1  
20. (Amended) The process for producing a treated manganese dioxide ore of Claim 19, wherein the device for mixing the ore with the reducing gas comprises one or more movable stirring blades installed in the kiln or one or more stirring blades fixed to the inner wall of the kiln.

21. (Amended) The process for producing a treated manganese dioxide ore of Claim 7, wherein the process is conducted continuously.

22. (Amended) The process for producing a treated manganese dioxide ore of Claim 8, wherein the process is conducted continuously.

23. (Amended) The process for producing a treated manganese dioxide ore of Claim 10, wherein the process is conducted continuously.

24. (Amended) The process for producing a treated manganese dioxide ore of Claim 10, wherein the reduced ore is cooled in a nonoxidizing atmosphere and then immersed in water.

25. (Amended) The process for producing a treated manganese dioxide ore of Claim 10, wherein the reduced ore is immersed in water and then cooled in a nonoxidizing atmosphere. then.

26. (Amended) The process for producing a treated manganese dioxide ore of Claim 24, wherein the reduced ore is continuously cooled.

27. (Amended) The process for producing a treated manganese dioxide ore of Claim 25, wherein the reduced ore is continuously cooled.

28. (Amended) The process for producing a treated manganese dioxide ore of Claim 10, wherein the immersion of the reduced ore in water is conducted so as to yield a slurry in which the concentration of the reduced ore [is] ranges from 10 to 40 % by weight.

29. (Amended) The process for producing a treated manganese dioxide ore of Claim 10, wherein the immersion of the reduced ore in water is conducted for a period [of] ranging from 1 to 24 hours.

30. (Amended) The process for producing a treated manganese dioxide ore of Claim 10, wherein the immersion of the reduced ore in water is conducted in one or more stirring tanks for continuous processing.

32. (Amended) A process for producing electrolytic manganese dioxide which comprises:

adding sulfuric acid to the treated manganese dioxide ore of Claim 1 or 5 to dissolve the ore, thereby preparing an aqueous solution of manganese sulfate;

purifying the aqueous solution of manganese sulfate; and then

subjecting the purified solution to electrolytic oxidation to oxidize the manganese sulfate.

33. (Amended) A process for producing electrolytic manganese dioxide which comprises:

preparing a treated manganese dioxide ore by the process of Claim 7;

adding sulfuric acid to the treated manganese ore to dissolve the ore, thereby preparing an aqueous solution of manganese sulfate;

purifying the aqueous solution of manganese sulfate; and then

subjecting the purified solution to electrolytic oxidation to oxidize the manganese sulfate.

34. (Amended) An electrolytic manganese dioxide which is used in batteries and which is prepared by:

dissolving the treated manganese dioxide ore of Claim 1 or 5 in sulfuric acid, thereby forming an acid manganese sulfate solution;

purifying the acid manganese sulfate solution; and

electrolytically oxidizing the manganese sulfate solution.--